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D.K.C. Hodgeman, F.J. Upsher
and L.E. Fletcher

DEPARTMENT OF DEFENCE

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ABSTRACT

This paper, the last in a series of four reports on an investigation into the environmental factors contributing to formation of hydrogen sulfide in shipboard oily-water waste, discusses approaches to minimising the problem. In particular, the importance of ensuring that the oily-water waste environment does not provide an optimal growth medium for sulfate-reducing bacteria, and that the quantities of sulfate available for reduction are kept as low as possible, are emphasised. Recommendations for changes to design and operating procedures which should achieve these aims are presented.

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Lyn Fletcher, BAppSc (Chem.) (RMIT) joined Aeronautical and Maritime Research Laboratory in 1985 and worked for three years on research into polymer and solvent interactions. She then joined a small multidisciplinary group investigating some environmental problems encountered by the Royal Australian Navy. In support of this work, Lyn is currently studying for a MEnvSc at Monash University.

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1. Introduction

The Royal Australian Navy has been experiencing problems with hydrogen sulfide forming in oily-water wastes in its ships. DSTO-AMRL has been conducting an investigation into the shipboard environmental factors contributing to generation of this gas in the waste. Previous reports have discussed the origin of the hydrogen sulfide (Hodgeman et al. 1995a), the microbiological aspects (Upsher et al., 1995), and the ship factors (Hodgeman et al., 1995b).

In this report, the last in the series, we consider some approaches to control of the hazard arising from generation of hydrogen sulfide in shipboard oily-water wastes. The discussion is based on the results presented in our other reports and on material obtained from the literature. In principle, we could eliminate the hazard by ensuring the absence of sulfur-containing substances or sulfate-reducing bacteria in the oily-water waste. Achieving either of these goals would be very difficult. Since hydrogen sulfide is only toxic at high concentrations (threshold limit value 10 ppm (Sax & Lewis, 1989)) it is not necessary to eliminate it entirely; the generation of some hydrogen sulfide could be tolerated provided that the oily-water waste environment was modified or managed to ensure that hazardous quantities of the gas cannot develop. Non-toxic concentrations of hydrogen sulfide in the air will severely degrade the quality of the working environment for the crew (the gas smells of "rotten eggs") but can also serve as a warning of the potential for development of a toxic gas hazard.

2. Background

Hydrogen sulfide gas is toxic at high concentrations and can present a serious safety hazard to a ship's crew if it reaches toxic levels in confined working areas. The magnitude that this hazard can reach was shown in the accident aboard HMAS Stalwart in 1985 in which three sailors lost their lives through hydrogen sulfide asphyxiation (RAN, 1986). The toxic atmosphere on that occasion resulted from spillage of a large quantity of oily-water waste which had been stored in the holding tank for some time.

Oily-water wastes are stored because of the need to comply with regulations introduced to protect the marine environment from pollution. The International Maritime Organisation regulations (IMO, 1985) allow a maximum oil content of 15 parts per million (ppm) in water discharged from ships in environmentally sensitive regions. If the oil content of the water exceeds this level the waste cannot be disposed of immediately but must be retained until suitable disposal facilities are available. This can result in a large quantity of oily-water waste being stored for an extended period. A destroyer, for example, might be carrying as much as 10 tonne of this waste in holding tanks. At the time of the accident, HMAS Stalwart was carrying 82 tonne of oily-water waste in a tank with a capacity of 90 tonne. The bulk of this waste is diluted sea-water containing detergents and other cleaning agents.

The hydrogen sulfide formed in shipboard oily-water wastes is generated by bacterial reduction of sulfate in the waste. The process requires anaerobic conditions and detailed discussions of the important factors are presented in other reports in this series (Hodgeman et al., 1995a; Upsher et al., 1995; Hodgeman et al., 1995b). Our experiments with a model oily-water waste (Hodgeman et al., 1995a) showed that hydrogen sulfide was not produced during the first few days of storage. This was the period during which the waste was becoming anaerobic and is consistent with the observation that hydrogen sulfide is generally found in shipboard oily-water wastes which have remained stagnant for some time. Thus, frequent disposal of the waste would prevent the formation of hydrogen sulfide and the possibility of a toxic atmosphere. Frequent disposal of the wastes is not always possible due to the presence of emulsified oil. Therefore, any ship storing large quantities of oily-water waste has the potential for formation of toxic quantities of hydrogen sulfide. Eliminating this hazard is an important aspect of ship safety.

3. Discussion & Conclusions

The oily-water waste in ships accumulates in two main locations - the bilges and the holding tank. The residence time of such wastes in bilges is generally quite short as the contents are routinely pumped into the holding tank via a common waste handling system. Ballast water from compensated fuel storage tanks is also pumped into the oily-water waste handling system. These handling systems usually incorporate a gravity separation device such as a plate separator or centrifuge to separate the oil and water components. If this equipment effectively separates these components much of the water layer can be discharged from the ship and the volume of the waste reduced. Emulsified oil is frequently encountered in the water layer of bilge due to the use of detergents in machinery space cleaning. These emulsions cannot be removed by the separation equipment in current use and the discharge of this component of the waste is therefore precluded. Under these circumstances the entire waste must be stored in the holding tank for later disposal.

Eliminating hydrogen sulfide requires identification of the main sources of the hazard. It also requires identification of the different stages of the oily-water waste handling procedure which offer an approach to removal of hydrogen sulfide or its precursors from the ship. A practical solution to the problem should require minimum changes to a ship's operating procedures, minimum modification of the ship, and should not introduce any further hazards to the crew. As a general rule, however, oily-water waste should not be stored unnecessarily. Every opportunity to dispose of the waste in an environmentally acceptable manner should be taken.

Before discussing approaches to minimising hydrogen sulfide formation a distinction must be made between "nuisance" levels and "hazard" levels of hydrogen sulfide in the air. The human nose is a very sensitive detector for hydrogen sulfide and responds to the gas at concentrations far below those which present any danger. Thus, the threshold limit value (TLV) for hydrogen sulfide is 10 ppm (Sax and Lewis, 1989) whereas the nose can

detect the smell of "rotten eggs" at concentrations down to 0.001 ppm (WHO, 1981). Most portable hydrogen sulfide monitors respond to concentrations in the 1-100 ppm range so that many investigations of complaints of hydrogen sulfide odours do not even lead to a reading on the detector. These are "nuisance" levels of hydrogen sulfide which merely degrade the quality of the workplace environment. Hydrogen sulfide begins to become acutely toxic at concentrations above 100 ppm and is invariably fatal at concentrations exceeding 1000 ppm (Sax & Lewis, 1989). Unfortunately, hydrogen sulfide causes olfactory paralysis at these toxic concentrations so that smell alone gives us no warning of a hazardous situation.

3.1 Ventilation

Forced air ventilation is the first approach which must be considered in dealing with the hydrogen sulfide problem. Engine rooms, boiler rooms and other machinery spaces in surface ships are generally well ventilated so that hydrogen sulfide concentrations in the bilge-water and air will be at "nuisance" levels only. A toxic hazard would be unlikely to develop in a well ventilated working machinery space. In our experience, the presence of hydrogen sulfide in the atmospheres of machinery spaces of surface ships is rare although this may not be the case for submarines. For surface ships, continuous forced ventilation with external fresh air is probably the most satisfactory method for ensuring that hydrogen sulfide does not present a hazard. Ventilation, coupled with regular removal of bilge (every two to three days), would eliminate any hazard from hydrogen sulfide produced in the machinery space itself. (A closed, unventilated machinery space containing bilge, however, should be treated with caution.) Fresh-air ventilation in submarines is not always possible and other approaches to managing hydrogen sulfide must be considered, particularly when they are submerged for extended periods. The presence of nuisance levels of hydrogen sulfide should not, however, be ignored as they suggest the waste has the potential to produce hazardous quantities of the gas during storage.

For stored wastes, forced ventilation of the headspace of a holding tank on a surface ship, either with air or inert exhaust gases, will remove the hydrogen sulfide gas from above the liquid. The gas remaining dissolved in the liquid will partition between the liquid and headspace so that continuous removal of the hydrogen sulfide by this method is possible. However, fresh oily-water waste is routinely added to the holding tank from the bilges and other sources. Hydrogen sulfide generation in the liquid of the holding tank is consequently a continuous process. For an anaerobic holding tank supporting a large population of sulfate-reducing bacteria the concentration of hydrogen sulfide in the liquid could reach a high level even with continuous removal from the headspace.

As was indicated in the accident aboard HMAS Stalwart, it is the liquid contents of the holding tank which present the main danger to the crew. A hydrogen sulfide-rich liquid in the holding tank may present no hazard as long as it remains in the tank. However, if it should be released suddenly into a working area through accident, equipment failure, or damage to the ship the hydrogen sulfide level in the atmosphere of the working area may rise rapidly to toxic levels. The ventilation system of the working area would probably be inadequate for dealing with such a sudden release. Thus, although forced ventilation of the

headspace of a holding tank will help to reduce hydrogen sulfide levels, it may not remove the potential hazard. It would be good practice, therefore, to treat all uncontrolled releases of oily-water waste from a holding tank as hazardous and to evacuate the area immediately, since exposure to high concentrations of hydrogen sulfide can be instantly fatal.

With hydrogen sulfide being continually blown from the headspace of a holding tank, location of the vents becomes an important consideration. External vents to the holding tank would need to be sited well away from air intakes for the ship's ventilation system to avoid the hydrogen sulfide entering the occupied part of the ship. Even if the hydrogen sulfide has been diluted to "nuisance" levels in the air the smell will be unpleasant and likely to cause the crew discomfort and concern for their safety. Scrubbing methods are available for removal of hydrogen sulfide from gas streams (Schaack & Chan, 1988; Schaack & Chan, 1989) which could probably be adapted to the ship environment, if necessary.

It must be emphasised that a hydrogen sulfide-rich waste stored in a holding tank presents a hazard not only to the crew but also to those operating a shore facility used for disposal of the contents of the tank. It would therefore be better to aim for oily-water wastes containing no more than safe quantities of hydrogen sulfide rather than to rely on the holding tank isolating the danger from the working environment in the ship.

3.2 Control of Sulfate-reducing Bacteria Populations

The hydrogen sulfide produced in oily-water waste is a product of the respiration of sulfate-reducing bacteria. These bacteria are widely distributed in the marine environment and enter the ship with sea-water. Estuary mud brought up with anchor chains would contain very high populations of sulfate-reducing bacteria. Keeping these bacteria out of a ship is not considered feasible. The rate at which hydrogen sulfide is produced in oily-water waste, however, will be related to the bacterial population and to the concentrations of essential minerals and nutrients in the waste. By keeping the concentrations of these substances low the rate of sulfate reduction and hydrogen sulfide generation will be reduced.

Oily-water waste is a complex environment containing a diverse population of microorganisms and chemical substrates that they use in their metabolic processes. The carbon cycle (Fig. 1) shows how the different types of bacteria use the available organic matter and the phosphate cycle (Fig. 2) shows how the bacteria use this important inorganic component. The bacterial populations that predominate at any particular time or location will depend on how well acclimatised the species have become to the conditions in the oily-water waste. The degree of oxygenation, pH, temperature and the nature of the organic and inorganic nutrients present in the waste will all affect the population levels of individual species.

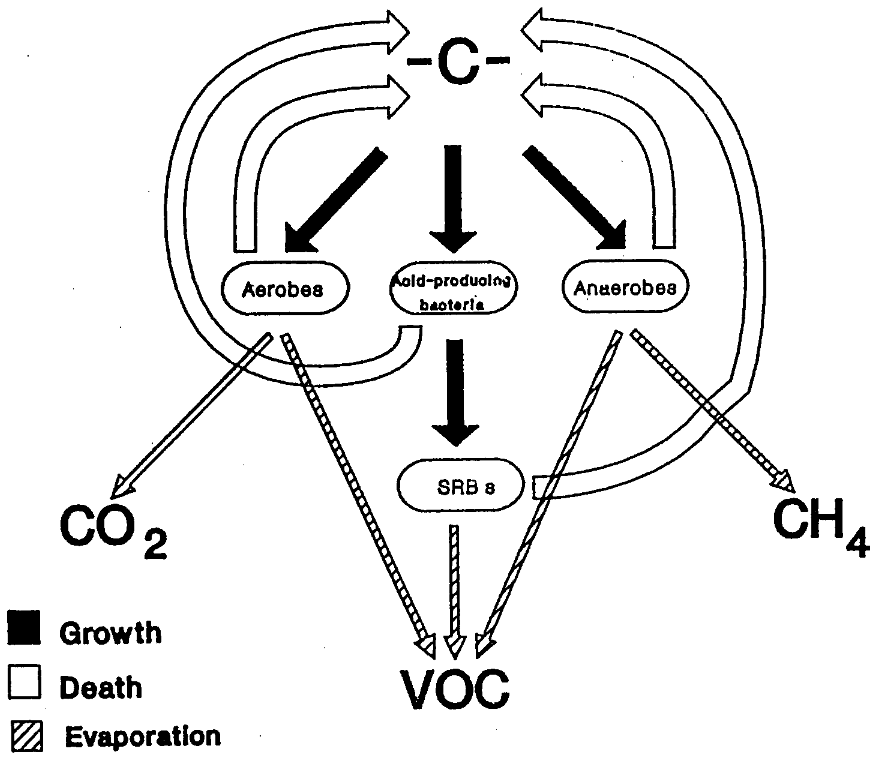

Fig. 1: Diagramatic representation of the cycling of carbon nutrients by the bacteria present in oily-water waste.

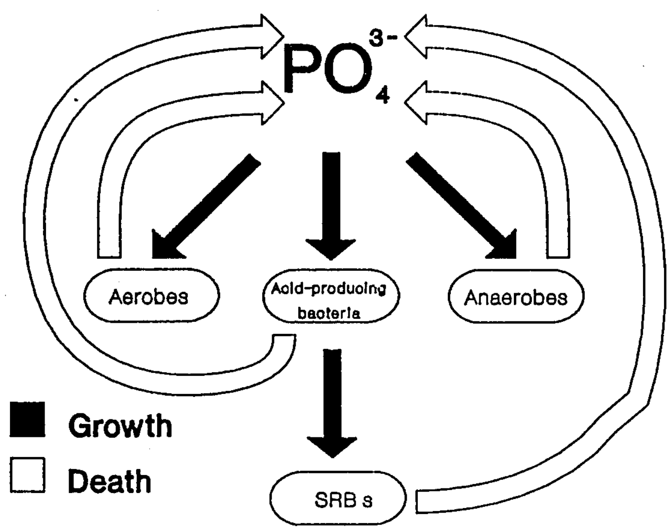

Fig. 2: Diagramatic representation of the cycling of phosphate by the bacteria present in oily-water waste.

Various modes of sterilisation have been suggested for controlling sulfate-reducing bacteria in ships. These include heat, chlorination, biocides, and irradiation with UV light or ionising radiation. Although these methods all find application in specific industries they would not be practical in a shipboard oily-water waste environment. Maintenance of a ship's bilges and holding tanks in a sterile state is an unrealistic objective. However, by keeping the sulfate-reducing bacteria populations low in the bulk oily-water waste (as opposed to surface biofilms and crevices, etc.) the rate of conversion of sulfate to hydrogen sulfide would be lowered. Approaches which should be considered are outlined below.

(a) Biocides

Although it is not practical to prevent entry of the sulfate-reducing bacteria into the ship, biocides could be used to control those that do. Such techniques are extensively used in the oil industry (Brunt, 1987; Maxwell et al., 1987) both in oil wells and in storage tanks. Use of biocides on ships would require the installation of dosing equipment and the development of safe-handling procedures as they are generally toxic substances. It should be noted that in the oil industry the ratio of oil to sea-water is often the opposite to that for oily-water waste in ships. Since the biocide will be partitioned between the two phases this will affect the amount of biocide required to achieve an effective concentration in the water layer. Development of resistant strains of bacteria and disposal of toxic biocide-containing oily-water waste would add further complications.

If an effective biocide which meets safety, cost and environmental considerations can be found then the use of biocides in the holding tank could be employed to reduce hydrogen sulfide formation. Since ventilation is sufficient for machinery spaces, biocides would only need to be used in the oily-water waste handling system and in the holding tank.

(b) Environment modification

The environmental conditions of the bilge-water could be manipulated to discourage growth of the sulfate-reducing bacteria. Aeration is widely used in other industrial waste environments and sewage treatment systems where these bacteria present a problem and is generally very effective if oxygen can be introduced faster than it is consumed by aerobic bacteria. Besides inhibiting growth of sulfate-reducing bacteria, aeration will also oxidise the hydrogen sulfide back to sulfate. A water-soluble cobalt complex has been reported to greatly increase the rate of oxidation of hydrogen sulfide in wastewater (Kotronarou & Hoffmann, 1991) at concentrations of the order of 1 g/tonne. Aeration must be considered one of the more practical approaches to controlling growth of the sulfate-reducing bacteria as it does not require the use of toxic or corrosive chemicals. A number of approaches are available for aeration of oily-water wastes and are discussed under the section on design considerations.

Other oxidants, such as hydrogen peroxide and peroxymonosulfate will oxidise hydrogen sulfide to sulfate (Betterton & Hoffmann, 1990) and prevent growth of

sulfate-reducing bacteria in wastes but could present handling and safety problems on a ship.

Adjustment of pH to levels outside the range in which these bacteria grow is another possible approach. The pH range favourable to growth of sulfate-reducing bacteria from RAN bilges is in the range 6 - 8. Lowering the pH by addition of acid would tend to enhance release of any hydrogen sulfide from the oily-water waste while raising the pH with alkali would keep the hydrogen sulfide in solution as the various sulfide anions. This approach would require the handling of concentrated acids or alkalis in the ship and may also cause corrosion problems.

(c) Nutrient deprivation

Removal of one or more of the nutrients essential to growth of the sulfate-reducing bacteria will prevent generation of hydrogen sulfide. Avoidance or minimisation of the addition of bulk organic nutrients such as biodegradable detergents and other organic matter to the waste is an important consideration. Separation of the water layer of the oily-water waste and disposal overboard would remove the prime source of sulfate required for hydrogen sulfide production along with other water soluble nutrients. This process is often prevented due to formation of oil-in-water emulsions that do not meet the IMO regulations for discharge. The use of non-emulsifying or fastbreak detergents or membrane filtration techniques would help overcome the emulsion problem.

Another approach is to ensure that the oily-water waste is deficient in an essential ingredient such as phosphate. Since sea-water contains only very low levels of phosphate this could be achieved by ensuring chemical substances such as detergents and other cleaning agents that find their way into the oily-water waste do not contain phosphate.

3.3 Design Considerations

(a) Reduce the sea-water content of oily-water waste

The primary source of the hydrogen sulfide is sulfate present in the oily-water waste. The sulfate is introduced with the sea-water which forms a major component of the typical waste. Other sulfur compounds are present as sulfonated detergents and organic sulfur compounds in the oil and may contribute to the total available sulfur after bacterial breakdown. Elimination of sulfur-containing substances from the waste would completely remove the hydrogen sulfide problem - if there is no sulfur, there can be no hydrogen sulfide. Achieving this aim, however, would be very difficult as sea-water is used in many processes aboard a ship as well as entering through leaks and hatches in rough seas. Removal of the sulfate by chemical reaction would not be practical. However, reducing the sea-water content of bilge and other oily-water wastes entering the holding tank would contribute to reducing the sulfate content of the waste and reduce the hydrogen sulfide hazard.

Ballast entering the oily-water waste handling system from compensated fuel tanks would probably consist almost entirely of sea-water. If this waste is free of detergents and separates readily into water and oil layers the opportunity to dispose of the water layer overboard should be taken (provided it meets regulations) rather than add it to the contents of the holding tank.

If separate waste handling systems for "dirty" oily-water waste (i.e., those in which the water layer contains emulsified oil) and "clean" oily-water waste (no emulsified oil) were installed, the amount of sea-water entering the holding tank could be reduced.

(b) Reduce the nutrient content of oily-water waste

Liquids entering the bilges come from a variety of sources. Some of these wastes, such as washdown water and overflow from galleys, etc., contain substantial quantities of organic nutrient which will contribute to hydrogen sulfide production if added to the holding tank. Since these wastes are "non-oily" they do not need to be handled by the oily-water waste system and should be diverted overboard or to the grey-water handling system as appropriate.

(c) Keep the oily-water waste well aerated

Sparging the contents of the holding tank with air would prevent the waste from becoming anaerobic, thereby providing an environment unsuitable for growth of sulfate-reducing bacteria. For this to be effective oxygen would need to enter the waste at a rate greater than it is consumed by aerobic bacteria in the waste. Efficient mixing of the waste would be necessary. Noise generated in sparging and mixing could present problems and would need to be considered.

Alternatively, instead of using one large holding tank the oily-water waste could be stored in a number of smaller tanks. By pumping the waste frequently from tank to tank, possibly with air injection into the pumped stream, the opportunity for the waste to become anaerobic would be reduced. Forced ventilation of the tanks with air would be required.

4. Recommendations

The hydrogen sulfide problem has resulted from efforts to protect the marine environment from pollution. Unfortunately, there is no single straightforward solution to the problem as the primary ingredients - sea-water and biodegradable detergents - are an essential part of a ship's operation. The solution would appear to lie in attention to oily-water waste management procedures and machinery space housekeeping practices. Elimination or

minimisation of the hydrogen sulfide problem will come from ensuring that the contents of the oily-water waste holding tank do not provide an optimal growth medium for sulfate-reducing bacteria. The following recommendations can be made:

(1) Review machinery space cleaning practices; clean machinery spaces with detergents when the ship is in port, preferably using fresh water; do not add the washings to the oily-water holding tank but, instead, pump them directly to a shore-based disposal facility; if possible, avoid the use of biodegradable detergents at sea to prevent their addition to the holding tank.

(2) Review drainage pathways of all nutrient-bearing "non-oily" wastes (washdown water from galleys, heads, etc.) and ensure they do not enter the oily-water waste system.

(3) Keep the sea-water content of the oily-water waste as low as possible; always use fresh water for cleaning operations when it is available; handle "emulsified" oily-water waste apart from "non-emulsified" oily-water waste so that separation equipment can be used effectively.

(4) Be aware of the chemical composition of cleaning agents and other substances entering bilge; use biodegradable detergents sparingly; avoid the addition of phosphates to the oily-water waste; DSTO advice should be sought before introduction of new cleaning agents.

(5) Prevent the oily-water waste from becoming anaerobic; remove bilge from machinery spaces frequently; keep the contents of the holding tank well aerated.

(6) Finally, do not store oily-water waste on a ship unnecessarily, dispose of it at every available opportunity.

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This paper, the last in a series of four reports on an investigation into the environmental factors contributing to formation of hydrogen sulfide in shipboard oily-water waste, discusses approaches to minimising the problem. In particular, the importance of ensuring that the oily-water waste environment does not provide an optimal growth medium for sulfate-reducing bacteria, and that the quantities of sulfate available for reduction are kept as low as possible, are emphasised. Recommendations for changes to design and operating procedures which should achieve these aims are presented.

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